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PATENT ABSTRACTS OF JAPAN(11)Publication number : **10-152595**(43)Date of publication of application : **09.06.1998**

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C08L 33/12**C08L 51/00**(21)Application number : **08-325959**(71)Applicant : **KURARAY CO LTD**(22)Date of filing : **21.11.1996**(72)Inventor : **NOKURA KOICHI
HOSHIBA TAKAO
OTANI MITSUO****(54) SHOCK-RESISTANT METHACRYLIC RESIN COMPOSITION**

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain the subject resin composition that is excellent in sheet or film-forming properties and processability and can give molding products having no wall thickness deviation and surface roughness and is useful in the optical fields by formulating a specific methacrylic polymer to a specific impact-resistant methacrylic polymer.

SOLUTION: (A) 90-99 pts.wt. of a impact-resistant methacrylic resin comprising a multilayer structure polymer prepared by grafting a rubber layer mainly of an alkyl acrylate (M1) and the resin layer mainly of an alkyl methacrylate (M2) or a multilayer structure polymer prepared by grafting a rubber layer mainly of a conjugated diolefin and the M1 monomer and the resin layer mainly of M2, and (B) a monomer mixture of 80-100wt.% of a 1-4C alkyl M2, 0-20wt.% of a 1-8C alkyl M1 and 0-10wt.% of other unsaturated monomers copolymerizable with them are subjected to emulsion polymerization to give the objective resin composition that contains 10-1 pts.wt. of a methacrylic polymer with a viscosity average molecular weight of 300,000-1,000,000.

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CLAIMS

[Claim(s)]

[Claim 1] The shock-proof methacrylic system resin constituent which consists of shock-proof methacrylic resin [1] 90 shown below - the 99 weight sections, and the methacrylic system polymer [2] 10 - 1 weight section.

Shock-proof methacrylic resin [1]: Shock-proof methacrylic resin which consists of a multilayer-structure-polymer which comes to carry out the graft of the resin layer which makes a subject the rubber layer which makes alkyl acrylate a subject, and alkyl methacrylate, and/or a multilayer-structure polymer which comes to carry out the graft of the resin layer which makes a subject the rubber layer which makes a conjugate diolefin and alkyl acrylate a subject, and alkyl methacrylate.

methacrylic system polymer [2]: -- the monomer mixture which consists of at least one sort of alkyl methacrylate of 80 - 100 % of the weight whose carbon numbers of an alkyl group are 1-4, 0 - 20 % of the weight of at least one sort of alkyl acrylate whose carbon numbers of an alkyl group are 1-8, and 0 - 10 % of the weight of other unsaturation monomers in which these and copolymerization are possible -- an emulsion polymerization -- carrying out -- becoming -- a viscosity average molecular weight -- 300,000- the methacrylic system polymer which are 3000 and 000

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] Especially this invention relates to the shock-proof methacrylic system resin constituent excellent in injection-molding nature, a sheet moldability, processability, etc. about a shock-proof methacrylic system resin constituent.

[0002]

[Description of the Prior Art] Since the moldability is good, although it has appearance transparent and colorless [methacrylic resin] and beautiful and the outstanding weatherability, and it is broadly used for electrical parts, such as a louver, a tail lamp, a lens, and a tableware, vehicles parts, an optical use, an ornament, miscellaneous goods, the signboard, etc., it is not necessarily enough, many the improvement and reforming are examined, and the intensity to a shock is produced commercially also as shock-proof methacrylic resin.

[0003] However, the multilayer-structure polymer particle which the shock-proof methacrylic resin of these marketing gives shock resistance although the target shock resistance is satisfied as it is does not carry out full compatibility at a surrounding melting resin phase. injection molding since it distributes by the particle shape and has influence to the fluidity -- setting -- a process condition and metal mold -- what the product satisfied by, and the bias of board thickness arising in sheet fabrication, film fabrication, or sheet processing, homogeneity's cutting low or phenomena, such as a surface dry area, arising is hard to be obtained from is the present condition [that surface faults, such as KUMORI, occur in the gate section of mold goods with a gate configuration etc.]

[0004]

[Problem(s) to be Solved by the Invention] Therefore, the above-mentioned fault produced although a multilayer-structure polymer particle exists therefore is canceled, a good injection-molded product is given, the bias of the board thickness in sheet fabrication, film fabrication, or sheet processing does not arise, but homogeneity is high and this invention aims at offering the shock-proof methacrylic system resin constituent with which a good product without a surface dry area etc. is obtained.

[0005]

[Means for Solving the Problem] As a result of inquiring wholeheartedly about the shock-proof methacrylic system resin excellent in injection-molding nature, a sheet, a film moldability, processability, etc., by carrying out addition mixture of the high-polymer methacrylic system polymer obtained by the specific shock-proof methacrylic system resin according to the emulsion polymerization, this invention persons find out that the above-mentioned purpose can be attained, and came to complete this invention.

[0006] That is, according to this invention, the shock-proof methacrylic system resin constituent which consists of shock-proof methacrylic system resin [1] 90 shown below - the 99 weight sections, and the methacrylic system polymer [2] 10 - 1 weight section can attain the above-mentioned technical problem.

Shock-proof methacrylic resin [1]: Shock-proof methacrylic resin which consists of a multilayer-structure polymer which comes to carry out the graft of the resin layer which makes a subject the rubber layer which makes alkyl acrylate a subject, and alkyl methacrylate, and/or a multilayer-structure polymer which comes to carry out the graft of the resin layer which makes a subject the rubber layer which makes a conjugate diolefin and alkyl acrylate a subject, and alkyl methacrylate.

methacrylic system polymer [2]: -- the monomer mixture which consists of at least one sort of alkyl methacrylate of 80 - 100 % of the weight whose carbon numbers of an alkyl group are 1-4, 0 - 20 % of the weight of at least one sort of alkyl acrylate whose carbon numbers of an alkyl group are 1-8, and 0 - 10 % of the weight of other unsaturation monomers in which these and copolymerization are possible -- an emulsion polymerization -- carrying out -- becoming -- a viscosity average molecular weight -- 300,000- the methacrylic system polymer which are 3000 and 000

[0007]

[Embodiments of the Invention] Hereafter, this invention is explained in detail.

[0008] What mixed the shock-proof methacrylic resin which consists of a multilayer-structure polymer which comes to carry out the graft of the resin layer which makes a subject the rubber layer which makes a subject the alkyl acrylate obtained according to an emulsion polymerization, and alkyl methacrylate, and/or a multilayer-structure polymer which comes to carry out the graft of the resin layer which makes a subject the rubber layer which makes a conjugate diolefin and alkyl acrylate a subject, and alkyl methacrylate as shock-proof methacrylic resin [1] used for this invention, and these and the hard methacrylic resin which be

mentioned later The thing of ** of a degree - ** is more specifically used preferably.

[0009] ** JP,54-18298,B, JP,55-27576,B, 50 - 99.9 % of the weight of alkyl acrylate represented by JP,55-94917,A etc., The rubber layer constituted considering the alkyl acrylate which consists of 0.1 to 0 - 49.9 % of the weight [of other copolymerization nature monochrome ethylenic unsaturated monomers], cross-linking monomer, and/or graft unity monomer 5 weight as a subject, For example, it comes to carry out the graft of the resin layer constituted considering 70 - 100 % of the weight of alkyl methacrylate, and the alkyl methacrylate which consists of 30 - 0 % of the weight of other copolymerization nature monochrome ethylenic unsaturated monomers as a subject. The multilayer-structure polymer of about 0.2-0.5 micrometers of particle diameters obtained according to an emulsion polymerization, or shock-proof methacrylic resin obtained by carrying out melting mixture of these and the hard methacrylic resin.

[0010] ** Are represented by JP,46-18491,B, JP,55-27576,B, etc. For example, a conjugate diolefin and 50 - 99.9 % of the weight of alkyl acrylate, The rubber layer constituted considering the conjugate diolefin which consists of 0.1 to 0 - 49.9 % of the weight [of other copolymerization nature monochrome ethylenic unsaturated monomers], cross-linking monomer, and/or graft unity monomer 5 weight, and alkyl acrylate as a subject, For example, it comes to carry out the graft of the resin layer which makes a subject 70 - 100 % of the weight of alkyl methacrylate, and the alkyl methacrylate which consists of 30 - 0 % of the weight of other copolymerization nature monochrome ethylenic unsaturated monomers. The multilayer-structure polymer of about 0.2-0.5 micrometers of particle diameters obtained according to an emulsion polymerization, or shock-proof methacrylic resin obtained by carrying out melting mixture of this and the hard methacrylic resin.

[0011] ** Shock-proof methacrylic resin which consists of combination of the shock-proof methacrylic resin obtained by carrying out melting mixture of the above-mentioned multilayer-structure polymer, or this and hard methacrylic resin.

[0012] The rate of the rubber layer which the above-mentioned multilayer-structure polymer means what generally consists of layer structures, such as a rubber layer / resin layer, a resin layer / rubber layer / resin layer, and a rubber layer / resin layer / rubber layer / resin layer, and is occupied to a polymer is usually 30 - 60% of the weight of a thing preferably 20 to 70% of the weight. As for the outermost layer of drum of a multilayer-structure polymer, it is desirable that it is the resin layer which makes alkyl methacrylate a subject from the point of melting miscibility with hard methacrylic resin or an methacrylic system polymer [2] etc.

[0013] Moreover, if it is general-purpose methacrylic resin usually used by the fabricating methods, such as an injection-molding method or an extrusion method, as the above-mentioned hard methacrylic resin, especially, it can be used without a limit, and will consist of 80 - 100 % of the weight of methyl methacrylate units, and 20 - 0% of the weight per sort [at least] of an alkyl acrylate unit whose carbon numbers of an alkyl group are 1-8, and that whose viscosity average molecular weight is 80,000 to about 200,000 will be used preferably. Although it is not limited but arbitrary polymerization methods can be adopted especially as the manufacture method of hard methacrylic resin, it is usually manufactured according to an emulsion polymerization, a suspension polymerization, etc. Moreover, especially the configuration may not have a limit, for example, which thing is sufficient as the shape of a particle of about 0.1-0.5 micrometers of particle diameters obtained by the emulsion polymerization, the shape of a bead of about 100-800 micrometers of particle diameters obtained by the suspension polymerization, the shape of a pellet which were acquired by extruding these and carrying out, etc. Usually, in case a latex blend is carried out in these, it is a particle-like, and in case a melting blend is carried out, mixture is presented by the shape of the shape of a bead, and a pellet.

[0014] the shock-proof methacrylic resin [1] 100 weight section which consists only of the above-mentioned multilayer-structure polymer as an amount of mixtures of the hard methacrylic resin in the shock-proof methacrylic system resin constituent of this invention -- receiving -- the 1 - 900 weight section -- the 100 - 600 weight section is preferably desirable As the mixed method of hard methacrylic resin, there is especially no limit, for example, mix to the above-mentioned shock-proof methacrylic resin [1]. Mix into the mixture of shock-proof methacrylic resin [1] and an methacrylic system polymer [2]. After mixing the part to shock-proof methacrylic resin [1] and/or an methacrylic system polymer [2], the method of mixing the shock-proof methacrylic resin [1], the methacrylic system polymer [2], and hard methacrylic resin which mix the remainder further together is employable.

[0015] In the shock-proof methacrylic system resin constituent of this invention, moreover, the methacrylic system polymer [2] which are other indispensable components 80 - 100 % of the weight of at least one sort of alkyl methacrylate whose carbon numbers of an alkyl group are 1-4, 0 - 20 % of the weight of at least one sort of alkyl acrylate whose carbon numbers of an alkyl group are 1-8, and the monomer mixture which consists of 0 - 10 % of the weight of other unsaturation monomers in which these and copolymerization are possible -- an emulsion polymerization -- carrying out -- becoming -- a viscosity average molecular weight -- 300,000- it is required to be the methacrylic system polymer which are 3000 and 000 what has the function to produce ***** with the matrix resin which makes melting phases, such as hard methacrylic resin, and to change flow behavior although the methacrylic system polymer [2] is unknown for details -- it is -- the addition -- if it carries out comparatively -- shock-proof methacrylic resin [1] 90 - 99 weight section -- receiving -- 10 - 1 weight section -- it is 7 - 2 weight section preferably The improvement effect of a moldability falls and has the fluidity of an addition hardly desirable in under 1 weight section, if there is no addition of an methacrylic system polymer and it exceeds 10 weight sections on the other hand.

[0016] As alkyl methacrylate used for the above-mentioned methacrylic system polymer [2], methyl methacrylate, ethyl methacrylate, butyl methacrylate, cyclohexyl methacrylate, etc. are mentioned, and especially methyl methacrylate is used preferably. As alkyl acrylate, methyl acrylate, ethyl acrylate, n-butyl acrylate, i-butyl acrylate, 2-ethylhexyl acrylate, etc. are mentioned, and styrene, an alpha methyl styrene, p-methyl styrene, acrylonitrile, a methacrylonitrile, etc. are mentioned as other unsaturation monomers in which these and copolymerization are possible, and they are used by independent or two sorts or more.

[0017] the viscosity average molecular weight of the above-mentioned methacrylic system polymer -- 300,000- 3000 and 000 -- it is -- more -- desirable -- 500 and 000- it is 2000 and 000 If about [that the improvement effect of a moldability is / a viscosity average molecular weight / low at less than 300,000] or a fluidity did not improve but it is over 3000 and 000 on the other hand, the improvement effect of a moldability falls and is not desirable. In the range with which this methacrylic system polymer is satisfied of this condition, it may not be, for example, a monolayer particle is sufficient, the double layer particle more than two-layer [which changed composition] is sufficient as especially restrictions, and they may also be the mixture of these particles. Although this methacrylic system polymer is obtained by the shape of a particle according to an emulsion polymerization, as for the particle diameter, it is more preferably desirable that it is 0.05-0.5 micrometers 0.03-1 micrometer, and, as for Tg (glass transition temperature) of an methacrylic system polymer, it is more preferably desirable that it is 80-110 degrees C 70-120 degrees C.

[0018] As a shock-proof methacrylic system resin constituent of this invention, after mixing uniformly the polymer latex or emulsion of the above-mentioned shock-proof methacrylic resin [1] and an methacrylic system polymer [2] with those states, you may be the mixture or melting mixture of mixture or these congelations, and the aforementioned hard methacrylic system resin of the congelation which carried out solidification separation by arbitrary methods, and was obtained by drying, the polymer latex of each polymer, or the congelation of an emulsion. In this way, the shock-proof methacrylic system resin constituent obtained is used as a molding material used for injection molding etc. in configurations, such as a pellet besides a congelation or melting mixture, and is processed into a sheet, a film, etc. by the extruder etc. in configurations, such as remaining as it is or a pellet. In a shock-proof methacrylic system resin constituent, the ultraviolet ray absorbent usually used for hard methacrylic resin, an antioxidant, lubricant, a stain pigment, etc. can be added if needed in the range which does not have trouble in the purpose of this invention.

[0019]

[Example] Next, this invention is not limited by these although an example explains this invention in detail. In addition, "%" and the "section" in an example meant "weight %" and the "weight section", and abbreviated names, such as a monomer to be used, a polymerization initiator, and a chain transfer agent, used the thing in the following parenthesis.

[0020] Methyl methacrylate (MMA), methyl acrylate (MA), ethyl acrylate (EA), n-butyl acrylate (bus available), styrene (ST), a butadiene (BD), allyl-compound methacrylate (ALMA), 1, 3-butylene-glycol dimethacrylate (BGDMA), potassium persulfate (KPS), n octyl mercaptan (n-OM)

[0021] Physical-properties evaluation of the resin constituent in an example etc. and evaluation of molding processability were measured according to the following method.

(1) It put in so that a particle-diameter latex might be diluted with pure water and it might become 1mm thick intensity as concentration 0.1 to 0.2% at an aluminum tray, and it dried at 80 degrees C, this was observed with the electron microscope, and the particle diameter was measured.

Electron microscope: JEOL Co., Ltd. make Scanning electron microscope model The limiting viscosity in 25 degrees C was measured and computed, using JSM-6300F(2) molecular-weight chloroform as a solvent.

[0022] (3) Glass transition temperature; it asked by the formula of TgFox. In addition, Tg of each monomer is a polymer handbook / Wiley. The value of interscience was used.

(4) Izod impactive strength (those with a notch)

It measured based on ASTM-D256.

(5) Heat deflection temperature; it measured based on HDTASTM-D648 (264psi).

(6) It measured based on all light transmissions and Hayes ASTM-D1003 (5mm **).

[0023] (7) the moldability and processability of an evaluation resin constituent of fabricating-operation nature pelletizing this, and fabricating 3mm mirror-plane plate with an injection molding machine -- moreover, 3mm ejector plate was manufactured with 90phi sheet extruder equipped with the mirror-plane roll of three, and it evaluated by thrusting up after heating this and subsequently, processing it

[0024] (Example 1)

(1) Having taught the ion-exchange-water 150 section, the sodium-stearate 0.4 section, and the lauryl sarcosine acid sodium 0.05 section to the reaction vessel with a manufacture reflux capacitor of a multilayer-structure polymer (A-1) latex, and stirring under nitrogen atmosphere, taught the monomer mixture which consists of the MMA24 section, the EA1 section, and the ALMA0.05 section after a temperature up, and 1%KPS solution 2.5 section to 80 degrees C, it was made to react for 60 minutes, and the polymerization was completed. Then, when the KPS solution 5 section is taught 1%, after carrying out continuation dropping of the monomer mixture which consists of the bus-available41.3 section, the ST8.7 section, and the ALMA1 section for 60 minutes and teaching the whole quantity, it held for 60 minutes and the polymerization was made to complete. subsequently, they are 2.5 ***** about 1%KPS solution -- carried out continuation dropping of the whole quantity the back, having applied the monomer mixture which consists of the MMA24 section, the MA1 section, and the n-OM0.05 section for 40 minutes, held for 60 more minutes, the polymerization was made to complete, and the multilayer-structure polymer (A-1) latex was obtained It checked that sampled the latex after a polymerization end of each class, there was no generation of a new particle at electron microscope observation, and successive polymerization was performed. The particle diameter of the obtained latex was 0.22 micrometers. Composition of this latex etc. is shown in (A-1) of Table 1.

[0025] (2) Having taught the ion-exchange-water 150 section, the sodium-stearate 1.2 section, and the lauryl sarcosine acid sodium 0.5 section to the reaction vessel with a manufacture reflux capacitor of a hard methacrylic resin (B-1) latex, and stirring

under nitrogen atmosphere, taught the monomer mixture which consists of the MMA47 section, the MA3 section, and the n-OM0.13 section after a temperature up, and 1%KPS solution 5 section to 75 degrees C, it was made to react for 60 minutes, and the polymerization was completed. Then, when the KPS solution 5 section is taught 1%, after carrying out continuation dropping of the monomer mixture which consists of the MMA47 section, the MA3 section, and the n-OM0.13 section for 60 minutes and teaching the whole quantity, it held for 60 minutes and the polymerization was made to complete. The particle diameter of the obtained latex was 0.12 micrometers. Composition of this latex etc. is shown in (B-1) of Table 1.

[0026] (3) Having taught the ion-exchange-water 150 section, the sodium-stearate 1.2 section, and the lauryl sarcosine acid sodium 0.5 section to the reaction vessel with a manufacture reflux capacitor of an methacrylic system polymer (C-1) latex, and stirring under nitrogen atmosphere, taught after a temperature up, the MMA25 section, and the 1%KPS solution 2 section to 65 degrees C, it was made to react for 90 minutes, and the polymerization was completed. Subsequently, when the KPS solution 7.5 section is taught 1%, after carrying out continuation dropping of the MMA75 section for 100 minutes and teaching the whole quantity, it held for 90 minutes and the polymerization was made to complete. The particle diameter of the obtained latex was 0.15 micrometers. Composition of this latex etc. was shown in (C-1) of Table 1.

[0027] Thus, after carrying out each obtained latex by polymer conversion and carrying out uniform mixture of the multilayer-structure polymer (A-1) 60 section, the hard methacrylic resin (B-1) 35 section, and the methacrylic system polymer (C-1) 5 section in the state of a latex, magnesium sulfate solution was added 2%, salting-out solidification was carried out, it rinsed and dried, and polymer powder was obtained. Uniform mixture of the polymer powder 100 obtained section and the below parapet EH [below [the grade for : extrusion molding by Kuraray Co., Ltd. and] (it is called D-1 for short)] 100 section which is a hard methacrylic system resin was carried out, it considered as the ejector plate with the sheet extruder, and measurement evaluation of many of the physical properties was carried out. The result is shown in Table 2.

[0028] (Example 2)

(1) Having taught the ion-exchange-water 150 section and the sodium-dioctyl-sulfosuccinate 0.2 section to the reaction vessel with a manufacture reflux capacitor of a multilayer-structure polymer (A-2) latex, and agitating under nitrogen atmosphere, taught the monomer mixture which consists of the MMA33 section, the MA2 section, and the ALMA0.15 section after a temperature up, and 1%KPS solution 3.5 section to 85 degrees C, it was made to react for 60 minutes, and the polymerization was completed. Then, when the KPS solution 4.5 section is taught 1%, after carrying out continuation dropping of the monomer mixture which consists of the bus-available36.5 section, the ST8.5 section, and the ALMA1 section for 60 minutes and teaching the whole quantity, it held for 60 minutes and the polymerization was made to complete. Subsequently, after teaching the KPS solution 2 section 1%, carried out continuation dropping of the whole quantity, having applied the monomer mixture which consists of the MMA19 section, the MA1 section, and the n-OM0.05 section for 40 minutes, held for 60 more minutes, the polymerization was made to complete, and the multilayer-structure polymer (A-2) latex was obtained. It checked that sampled the latex after a polymerization end of each class, there was no generation of a new particle at electron microscope observation, and successive polymerization was performed. The particle diameter of the obtained latex was 0.15 micrometers. Composition of this latex etc. was shown in (A-2) of Table 1.

[0029] (2) Having taught the ion-exchange-water 150 section and the sodium-dioctyl-sulfosuccinate 0.6 section to the reaction vessel with a manufacture reflux capacitor of a hard methacrylic resin (B-2) latex, and stirring under nitrogen atmosphere, taught after a temperature up, the MMA18 section, the EA2 section, the n-OM0.05 section, and the 1%KPS solution 2 section to 80 degrees C, it was made to react for 40 minutes, and the polymerization was completed. Then, when the KPS solution 8 section is taught 1%, after carrying out continuation dropping of the monomer mixture which consists of the MMA72 section, the EA8 section, and the n-OM0.2 section for 90 minutes and teaching the whole quantity, it held for 60 minutes and the polymerization was made to complete. The particle diameter of the obtained latex was 0.07 micrometers. Composition of this latex etc. was shown in (B-2) of Table 1.

[0030] (3) Having taught the ion-exchange-water 150 section and the sodium-dioctyl-sulfosuccinate 0.5 section to the reaction vessel with a manufacture reflux capacitor of an methacrylic system polymer (C-2) latex, and stirring under nitrogen atmosphere, taught the monomer mixture which consists of the MMA27 section, the MA3 section, and the n-OM0.006 section after a temperature up, and 1%KPS solution 3 section to 75 degrees C, it was made to react for 60 minutes, and the polymerization was completed. Subsequently, when the KPS solution 7 section is taught 1%, after carrying out continuation dropping of the monomer mixture which consists of the MMA63 section, the EA7 section, and the n-OM0.014 section for 100 minutes and teaching the whole quantity, it held for 60 minutes and the polymerization was made to complete. The particle diameter of the obtained latex was 0.12 micrometers. Composition of this latex etc. was shown in (C-2) of Table 1.

[0031] Thus, after carrying out each obtained latex by polymer conversion and carrying out uniform mixture of the multilayer-structure polymer (A-2) 80 section, the hard methacrylic resin (B-2) 15 section, and the methacrylic system high-polymer (C-2) 5 section in the state of a latex, freezing was carried out over 3 hours at -40 degrees C, ice was dissolved in 75-degree C warm water, subsequently it dehydrated and dried, and polymer powder was obtained. Uniform mixture of the 100 [are called for short the grade for : injection molding by Kuraray Co., Ltd. and the following (D-2)] section which is the polymer powder 100 section and the hard methacrylic system resin which were obtained was carried out, it was pelletized, and injection-molding evaluation and many physical properties were evaluated. [parapet HR-L] The result is shown in Table 2.

[0032] (Examples 3-8) By the same method as an example 1, the multilayer-structure polymer [from which a number of layers, composition, and a particle diameter differ, respectively] (A-3) - (A-6) latex, and hard methacrylic resin (B-3) latex, and the methacrylic system polymer (C-3) latex were obtained. The number of layers of these polymers, composition, a particle diameter,

etc. are shown in Table 1. The injection-molding plate and ejector plate which the mixed rate with the mixed rate of each polymer in a latex blend, pelletizing, and the hard methacrylic system resin at the time of sheet-izing etc. was shown in Table 2, and also were obtained like the example 1 were measured and evaluated. The result was shown in Table 2.

[0033] (Examples 1-3 of comparison) It is obtained and it is inside **** which generating of a fault is accepted and satisfies when the mixed rate of each polymer in a latex blend deviates from the claim of this invention, although the multilayer-structure polymer latex in an example, the hard methacrylic resin latex, and the methacrylic system polymer latex were used. The result was shown in Table 2.

[0034] (Example 4 of comparison) It is obtained and it is inside **** which obtains an methacrylic system polymer (C-4) latex with small molecular weight by the same method as an example, and generating of a fault is accepted and the multilayer-structure polymer latex in this and an example and a hard methacrylic resin latex, and blend ** satisfy. The result was shown in Table 2.

[0035]

[Table 1]

| | 多層構造重合体 (A), 硬質メタクリル樹脂 (B), メタクリル系重合体 (C) の組成 [部] | 粒子径 [μm] | 分子量 ($\times 10^{-4}$) / Tg (°C) |
|-------|---|-------------|------------------------------------|
| (A-1) | MMA-EA-ALMA/BA -ST-ALMA/MMA-MA-n-OM 24 -1 -0.05/41.3-8.7-1 /24 -1 -0.05 | 0.22 | — |
| (A-2) | MMA-MA-ALMA/BA -ST-ALMA/MMA-MA-n-OM 33 -2 -0.15/38.5-8.5-1 /19 -1 -0.05 | 0.15 | — |
| (A-3) | BA -ST-ALMA/MMA-MA-n-OM 49.2-10.8-1 /38-2 -0.08 | 0.08 | — |
| (A-4) | MMA-ALMA/BA-ST-ALMA/MMA-BA-ST-EGDMA/MMA-MA-n-OM 25 -0.1 /41-9 -1 /4 -5 -1 -0.05 /14 -1 -0.03 | 0.31 | — |
| (A-5) | MMA-BA-ALMA/MMA-BA-n-OM 24 -6 -0.2 /62-8 -0.35 | 0.06 | — |
| (A-6) | BA-BD/MMA-MA-n-OM 30-20/48 -2 -0.1 | 0.08 | — |
| (B-1) | MMA-MA-n-OM/MMA-MA-n-OM 47 -3 -0.13/47 -3 -0.13 | 0.12 | — |
| (B-2) | MMA-EA-n-OM/MMA-EA-n-OM 18 -2 -0.05/72 -8 -0.2 | 0.07 | — |
| (B-3) | MMA-MA-n-OM/MMA-MA-n-OM 39 -1 -0.16/58.5-1.5-0.24 | 0.18 | — |
| (C-1) | MMA/MMA 25 /75 | 0.15 | 18000/105 |
| (C-2) | MMA-MA-n-OM /MMA-MA-n-OM 27 -3 -0.008/83 -7 -0.014 | 0.12 | 4400/92 |
| (C-3) | MMA-EA/MMA-EA 22 -3 /66 -9 | 0.08 | 11000/83 |
| (C-4) | MMA-MA-n-OM /MMA-MA-n-OM 24 -1 -0.02 /72 -3 -0.06 | 0.19 | 2700/100 |

[table Naka and the horizontal line (-) were used in order to distinguish the monomer used in order to form the same layer, and the slash (/) was used in order to show that layers differ.]

[0036]

[Table 2]

| | ラテックスブレンド | | | 押出溶融ブレンド | | Isod | HDT | 全光線 | ヘイズ | 成形性または加工性の評価 |
|-------|-------------|-------------|-------------|------------|--------------|--------------------|------|------------|-----|---------------------------------------|
| | (A) [部] | (B) [部] | (C) [部] | (C) [部] | (D) [部] | 衝撃強度 [kg-cu/cm] | [°C] | 透過率 [%] | [%] | |
| 実施例 1 | (A-1) 60 | (B-1) 35 | (C-1) 5 | — | (D-1) 200 | 4.1 | 98 | 92 | 1 | サージングなくシート成形性良好 突上げコーナー部の均一性良好 |
| 実施例 2 | (A-2) 80 | (B-2) 10 | (C-2) 10 | — | (D-2) 100 | 7.2 | 96 | 92 | 1 | 射出成形性良好： ゲート部欠点なし |
| 実施例 3 | (A-3) 98 | — | (C-3) 2 | — | (D-2) 70 | 9.8 | 83 | 92 | 1 | 射出成形性良好： ゲート部欠点なし |
| 実施例 4 | (A-4) 40 | (B-3) 56 | (C-2) 4 | — | — | 5.5 | 85 | 92 | 1 | 射出成形性良好： ゲート部欠点なし |
| 実施例 5 | (A-1) 70 | (B-1) 30 | — | (C-1) 5 | (D-2) 95 | 6.4 | 90 | 92 | 1 | 射出成形性良好： ゲート部欠点なし |
| 実施例 6 | (A-1) 70 | (B-1) 20 | (C-1) 10 | — | (D-1) 200 | 2.1 | 92 | 92 | 1 | サージングなくシート成形性良好 突上げコーナー部の均一性良好 |
| 実施例 7 | (A-5) 97 | — | (C-3) 3 | — | — | 3.1 | 58 | 91 | 2 | サージングなくシート成形性良好 突上げコーナー部の均一性良好 |
| 実施例 8 | (A-6) 80 | (B-1) 15 | (C-3) 5 | — | (D-2) 100 | 13.4 | 90 | 92 | 1 | 射出成形性良好： ゲート部欠点なし |
| 比較例 1 | (A-1) 60 | (B-1) 40 | — | — | (D-1) 200 | 3.9 | 94 | 92 | 1 | シート成形時サージング発生しやすい 突上げコーナーエッジ部均一性低下 |
| 比較例 2 | (A-2) 80 | (B-2) 20 | — | — | (D-2) 100 | 6.8 | 89 | 92 | 1 | 射出成形性： ゲート部クモリ欠点発生 |
| 比較例 3 | (A-3) 75 | — | (C-2) 25 | — | (D-2) 50 | 6.5 | 78 | 92 | 1 | 射出成形性： 流動性低下、成形不良 |
| 比較例 4 | (A-1) 80 | (B-1) 30 | (C-4) 10 | — | (D-2) 200 | 4.2 | 98 | 92 | 1 | 射出成形性： ゲート部クモリ欠点発生 |

[0037]

[Effect of the Invention] as mentioned above -- since the above-mentioned composition is used for the shock-proof methacrylic system resin constituent of this invention -- injection molding -- setting -- a process condition and metal mold -- in sheet fabrication, film fabrication, or sheet processing, surface faults', such as KUMORI, do not have generating in the gate section of mold goods by the gate configuration etc., and homogeneity is [there are few bias of board thickness and] high, and a good product without a surface dry area etc. can be offered, and it is suitably used in various fabrication

[Translation done.]

L17 ANSWER 67 OF 245 CA COPYRIGHT 2003 ACS

AN 129:123313 CA

TI Impact-resistant methacrylic resin compositions with good moldability and processability

IN Nokura, Koichi; Hoshiba, Takao; Otani, Mitsuo

PA Kuraray Co., Ltd., Japan

SO Jpn. Kokai Tokkyo Koho, 8 pp.

CODEN: JKXXAF

DT Patent

LA Japanese

IC ICM C08L033-12

ICS C08L051-00

CC 37-6 (Plastics Manufacture and Processing)

FAN.CNT 1

| | PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|------|----------------|------|----------|-----------------|----------|
| PI | JP 10152595 | A2 | 19980609 | JP 1996-325959 | 19961121 |
| PRAI | JP 1996-325959 | | 19961121 | | |

AB Title compns. comprise (1) 90-99 parts impact-resistant methacrylic resins

from (a) multilayer polymers prepd. by grafting alkyl acrylate-based rubber layers and alkyl methacrylate-based polymer layers and/or (b) multilayer polymers prepd. by grafting conjugated diolefin/alkyl acrylate-based rubber layers and alkyl methacrylate-based polymer layers and (2) 1-10 parts methacrylic polymers [viscosity-av. mol. wt. 300,000-3,000,000] prepd. by emulsion-polymerization. monomer mixts. contg. 80-100% .gtoreq.1 C1-4 alkyl methacrylates, 0-20% .gtoreq.1 C1-8 alkyl acrylates, and 0-10% other unsatd. monomers. Thus, a compn. contg. a 3-layer polymer [composed of 1st layer from Me methacrylate (I)/Et acrylate/allyl methacrylate (II) (24/1/0.05) mixt., 2nd layer from Bu acrylate/styrene/II (41.3/8.7/1) mixt, and 3rd layer from I/Me acrylate (III) (24/1) mixt.] 60, a rigid polymer (prepd. from 94 parts I and 6 parts III) 35, I homopolymer 5, and Parapet EH 100 parts showed good impact resistance, moldability, and processability.

ST impact resistance methacrylic resin blend; moldability processability methacrylic resin blend

IT Impact-resistant materials

(impact-resistant methacrylic resin compns. with good moldability and processability)

IT Polymer blends

RL: PRP (Properties); TEM (Technical or engineered material use); USES (Uses)

(impact-resistant methacrylic resin compns. with good moldability and processability)

IT 9010-88-2P, Ethyl acrylate-methyl methacrylate copolymer 107052-86-8P, Allyl methacrylate-butyl acrylate-methyl methacrylate graft copolymer 110254-00-7P, Allyl methacrylate-butyl acrylate-methyl acrylate-methyl methacrylate-styrene graft copolymer 150732-38-0P, Allyl methacrylate-butyl acrylate-1,3-butylene glycol dimethacrylate-methyl acrylate-methyl methacrylate-styrene graft copolymer 156697-84-6P, Butadiene-butyl acrylate-methyl acrylate-methyl methacrylate graft copolymer 205237-33-8P, Allyl methacrylate-butyl acrylate-ethyl acrylate-methyl acrylate-methyl methacrylate-styrene graft copolymer
RL: IMF (Industrial manufacture); POF (Polymer in formulation); PRP (Properties); TEM (Technical or engineered material use); PREP (Preparation); USES (Uses)

(impact-resistant methacrylic resin compns. with good moldability and processability)

IT 9011-14-7, Parapet EH 9011-87-4, Parapet HR-L
RL: POF (Polymer in formulation); PRP (Properties); TEM (Technical or
engineered material use); USES (Uses)
(impact-resistant methacrylic resin compns. with good moldability and
processability)

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(54) 【発明の名称】 耐衝撃性メタクリル系樹脂組成物

(57) 【要約】

【課題】 成形性および加工性に優れた耐衝撃性メタクリル系樹脂組成物を提供する。

【解決手段】 多層構造重合体からなる耐衝撃性メタクリル樹脂90～99重量部と、粘度平均分子量300,000～3,000,000のメタクリル系乳化重合体10～1重量部とよりなる。

【特許請求の範囲】

【請求項1】 下記に示される耐衝撃性メタクリル樹脂〔1〕90～99重量部と、メタクリル系重合体〔2〕10～1重量部からなる耐衝撃性メタクリル系樹脂組成物。

耐衝撃性メタクリル樹脂〔1〕：アルキルアクリレートとを主体とするゴム層とアルキルメタクリレートとを主体とする樹脂層をグラフトしてなる多層構造重合体、および／または共役ジオレフィンとアルキルアクリレートとを主体とするゴム層とアルキルメタクリレートとを主体とする樹脂層をグラフトしてなる多層構造重合体からなる耐

衝撃性メタクリル樹脂。
メタクリル系重合体〔2〕：アルキル基の炭素数が1～4である少なくとも1種のアルキルメタクリレート80～100重量%、アルキル基の炭素数が1～8である少なくとも1種のアルキルアクリレート0～20重量%、およびこれらと共重合可能な他の不飽和単量体0～10重量%からなる単量体混合物を乳化重合してなり、粘度平均分子量が300,000～3000,000であるメタクリル系重合体。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、耐衝撃性メタクリル系樹脂組成物に関し、特に射出成形性、シート成形性・加工性等に優れた耐衝撃性メタクリル系樹脂組成物に関する。

【0002】

【従来の技術】メタクリル樹脂は、無色透明で美しい外観と優れた耐候性を有し、また成形性が良好なことから、ルーバー、テールランプ、レンズ、テーブルウェア等電気部品、車両部品、光学用途、装飾、雑貨、看板などに幅広く用いられているが、衝撃に対する強度は必ずしも充分ではなく、その改良、改質が数多く検討され、耐衝撃性メタクリル樹脂としても製品化されている。

【0003】しかしながら、これら市販の耐衝撃性メタクリル樹脂は目的とする耐衝撃性はそれなりに満足されるものの、耐衝撃性を付与する多層構造重合体微粒子がまわりの溶融樹脂相に完全相溶するのではなく粒子形状で分散し、流動性に影響を有していることから、射出成形においては成形条件、金型ゲート形状等により成形品のゲート部にクモリ等の表面欠点が発生したり、またシート成形、フィルム成形あるいはシート加工において板厚の偏りが生じて均一性が低くかったり、あるいは表面荒れ等の現象が生じたりすることがあり、満足される製品が得られにくいのが現状である。

【0004】

【発明が解決しようとする課題】したがって、本発明は、多層構造重合体微粒子が存在するがゆえに生ずる上記欠点を解消し、良好な射出成形品を与え、シート成

形、フィルム成形あるいはシート加工での板厚の偏りが生じず均一性が高く、表面荒れ等のない良好な製品が得られる耐衝撃性メタクリル系樹脂組成物を提供することを目的とする。

【0005】

【課題を解決するための手段】本発明者らは、射出成形性、シート、フィルム成形性・加工性等に優れた耐衝撃性メタクリル系樹脂に関し鋭意研究した結果、特定の耐衝撃性メタクリル系樹脂に乳化重合により得られた高重合度のメタクリル系重合体を添加混合することにより、上記目的が達成できることを見出し、本発明を完成するに至った。

【0006】即ち、上記課題は本発明によれば、下記に示される耐衝撃性メタクリル系樹脂〔1〕90～99重量部と、メタクリル系重合体〔2〕10～1重量部からなる耐衝撃性メタクリル系樹脂組成物により達成することができる。

耐衝撃性メタクリル樹脂〔1〕：アルキルアクリレートとを主体とするゴム層とアルキルメタクリレートとを主体とする樹脂層をグラフトしてなる多層構造重合体、および／または共役ジオレフィンとアルキルアクリレートとを主体とするゴム層とアルキルメタクリレートとを主体とする樹脂層をグラフトしてなる多層構造重合体からなる耐

衝撃性メタクリル樹脂。
メタクリル系重合体〔2〕：アルキル基の炭素数が1～4である少なくとも1種のアルキルメタクリレート80～100重量%、アルキル基の炭素数が1～8である少なくとも1種のアルキルアクリレート0～20重量%、およびこれらと共重合可能な他の不飽和単量体0～10重量%からなる単量体混合物を乳化重合してなり、粘度平均分子量が300,000～3000,000であるメタクリル系重合体。

【0007】

【発明の実施の形態】以下、本発明について詳細に説明する。

【0008】本発明に用いる耐衝撃性メタクリル樹脂〔1〕としては、乳化重合によって得られる、アルキルアクリレートとを主体とするゴム層とアルキルメタクリレートとを主体とする樹脂層をグラフトしてなる多層構造重合体、および／または共役ジオレフィンとアルキルアクリレートとを主体とするゴム層とアルキルメタクリレートとを主体とする樹脂層をグラフトしてなる多層構造重合体からなる耐衝撃性メタクリル樹脂、およびこれらと後述する硬質メタクリル樹脂とを混合したものが挙げられる。より具体的には、例えば次の①～③のものが好ましく使用される。

【0009】①特公昭54-18298号公報、特公昭55-27576号公報、特開昭55-94917号公報などに代表される、例えばアルキルアクリレート50～99.9重量%、他の共重合性モノエチレン性不飽和

単量体0~49.9重量%、架橋性単量体および/またはグラフト結合性単量体0.1~5重量%からなるアルキルアクリレートとを主体として構成されるゴム層と、例えばアルキルメタクリレート70~100重量%、他の共重合性モノエチレン性不飽和単量体30~0重量%からなるアルキルメタクリレートとを主体として構成される樹脂層をグラフトしてなり、乳化重合によって得られる粒子径0.2~0.5 μ m程度が多層構造重合体、もしくはこれらと硬質メタクリル樹脂とを溶融混合して得られる耐衝撃性メタクリル樹脂。

【0010】の特公昭46-18491号公報、特公昭55-27576号公報などに代表される、例えば共役ジオレフィンとアルキルアクリレート50~99.9重量%、他の共重合性モノエチレン性不飽和単量体0~49.9重量%、架橋性単量体および/またはグラフト結合性単量体0.1~5重量%からなる共役ジオレフィンとアルキルアクリレートとを主体として構成されるゴム層と、例えばアルキルメタクリレート70~100重量%、他の共重合性モノエチレン性不飽和単量体30~0重量%からなるアルキルメタクリレートとを主体とする樹脂層をグラフトしてなり、乳化重合によって得られる粒子径0.2~0.5 μ m程度が多層構造重合体、もしくはこれと硬質メタクリル樹脂とを溶融混合して得られる耐衝撃性メタクリル樹脂。

【0011】⑤上記多層構造重合体またはこれと硬質メタクリル樹脂とを溶融混合して得られる耐衝撃性メタクリル樹脂の組み合わせからなる耐衝撃性メタクリル樹脂。

【0012】上記多層構造重合体とは、一般にゴム層/樹脂層、樹脂層/ゴム層/樹脂層、ゴム層/樹脂層/ゴム層/樹脂層などの層構造からなるものをいい、重合体に占めるゴム層の割合が通常20~70重量%、好ましくは30~60重量%のものである。多層構造重合体の最外層は、硬質メタクリル樹脂あるいはメタクリル系重合体[2]との溶融混合性の点などから、アルキルメタクリレートとを主体とする樹脂層であることが望ましい。

【0013】また、上記硬質メタクリル樹脂としては、射出成形法あるいは押出成形法などの成形法で通常用いられる汎用のメタクリル樹脂であれば特に制限なく使用することができ、メチルメタクリレート単位80~100重量%とアルキル基の炭素数が1~8であるアルキルアクリレート単位の少なくとも1種20~0重量%からなり、粘度平均分子量が80,000~200,000程度のものが好ましく用いられる。硬質メタクリル樹脂の製造方法としては、特に限定されず、任意の重合方法が採用できるが、通常乳化重合、懸濁重合などによって製造される。またその形状は、特に制限なく、例えば乳化重合で得られる粒子径0.1~0.5 μ m程度の微粒子状、懸濁重合で得られる粒子径100~800 μ m程度のビーズ状、これらを押出しして得られたペレット状

などいずれのものでもよい。通常、これらの中でラテックスブレンドする際には微粒子状で、また溶融ブレンドする際にはビーズ状またはペレット状で混合に供される。

【0014】本発明の耐衝撃性メタクリル系樹脂組成物における硬質メタクリル樹脂の混合量としては、上記多層構造重合体のみからなる耐衝撃性メタクリル樹脂

[1]100重量部に対し、1~900重量部、好ましくは100~600重量部が望ましい。硬質メタクリル樹脂の混合方法としては、特に制限はなく、例えば上記耐衝撃性メタクリル樹脂[1]に混合する、耐衝撃性メタクリル樹脂[1]、メタクリル系重合体[2]の混合物に混合する、耐衝撃性メタクリル樹脂[1]および/又はメタクリル系重合体[2]にその一部を混合した後

に更に残りを混合する、耐衝撃性メタクリル樹脂[1]、メタクリル系重合体[2]および硬質メタクリル樹脂と一緒に混合するなどの方法が採用できる。

【0015】また、本発明の耐衝撃性メタクリル系樹脂組成物において他の必須成分であるメタクリル系重合体[2]は、アルキル基の炭素数が1~4である少なくとも1種のアルキルメタクリレート80~100重量%、アルキル基の炭素数が1~8である少なくとも1種のアルキルアクリレート0~20重量%、およびこれらと共重合可能な他の不飽和単量体0~10重量%からなる単量体混合物を乳化重合してなり、粘度平均分子量が300,000~3000,000であるメタクリル系重合体であることが必要である。メタクリル系重合体[2]は、詳細は未詳であるが、硬質メタクリル樹脂などの溶融相をなすマトリックス樹脂との絡まりを生じて流動挙動を変化させる機能を有するものであり、その添加割合としては、耐衝撃性メタクリル樹脂[1]90~99重量部に対して、10~1重量部、好ましくは7~2重量部である。メタクリル系重合体の添加量が、1重量部未満では成形性の改良効果はほとんどなく、一方10重量部を超えると流動性が低下し好ましくない。

【0016】上記メタクリル系重合体[2]に用いるアルキルメタクリレートとしては、メチルメタクリレート、エチルメタクリレート、ブチルメタクリレート、シクロヘキシルメタクリレートなどが挙げられ、特にメチルメタクリレートが好ましく用いられる。アルキルアクリレートとしては、メチルアクリレート、エチルアクリレート、n-ブチルアクリレート、i-ブチルアクリレート、2-エチルヘキシルアクリレート等が挙げられ、またこれらと共重合可能な他の不飽和単量体としては、スチレン、 α -メチルスチレン、p-メチルスチレン、アクリロニトリル、メタクリロニトリル等が挙げられ、それらは単独または2種以上で用いられる。

【0017】上記メタクリル系重合体の粘度平均分子量は、300,000~3000,000であり、より好ましくは500,000~2000,000である。粘

度平均分子量が300,000未満では、成形性の改良効果が低いばかりか流動性が向上せず、一方3000,000を超えると成形性の改良効果が低下し好ましくない。このメタクリル系重合体は、この条件を満足する範囲において特に制約はなく、例えば単層粒子でもよいし、組成を変更した2層以上の複層粒子でもよいし、またこれらの粒子の混合物でもあってもよい。このメタクリル系重合体は、乳化重合により微粒子状で得られるが、その粒子径は0.03~1 μ m、より好ましくは0.05~0.5 μ mであることが望ましく、またメタ

クリル系重合体のTg(ガラス転移温度)は、70~120℃、より好ましくは80~110℃であることが望ましい。

【0018】本発明の耐衝撃性メタクリル系樹脂組成物としては、上記耐衝撃性メタクリル樹脂[1]、メタクリル系重合体[2]の重合体ラテックスまたはエマルジョンをそれらの状態のまま均一に混合した後、任意の方法により凝固分離し乾燥して得られた凝固物、それぞれの重合体の重合体ラテックスまたはエマルジョンの凝固物の混合物、あるいはこれら凝固物と前記硬質メタクリル系樹脂との混合物もしくは熔融混合物であってもよい。こうして得られる耐衝撃性メタクリル系樹脂組成物は、凝固物または熔融混合物のほか、ペレット等の形状で射出成形などに用いられる成形材料として使用されたり、またそのまままたはペレット等の形状で押出機などによりシート、フィルムなどに加工される。耐衝撃性メタクリル系樹脂組成物には、硬質メタクリル樹脂に通常用いられる紫外線吸収剤、酸化防止剤、滑剤、染料等を、本発明の目的に支障のない範囲で必要に応じて添加することができる。

【0019】

【実施例】次に本発明を実施例により詳細に説明するが、本発明はこれらによって限定されるものではない。なお、実施例における「%」および「部」は「重量%」および「重量部」を意味し、使用する単量体、重合開始剤、連鎖移動剤等の略称は下記カッコ内のものを用いた。

【0020】メチルメタクリレート(MMA)、メチルアクリレート(MA)、エチルアクリレート(EA)、n-ブチルアクリレート(BA)、スチレン(ST)、ブタジエン(BD)、アリルメタクリレート(ALMA)、1,3-ブチレンジグリコールジメタクリレート(BGDMA)、過硫酸カリウム(KPS)、n-オクチルメルカプタン(n-OM)

【0021】実施例中の樹脂組成物等の物性評価および成型加工性の評価は下記の方法に従い測定した。

(1) 粒子径

ラテックスを純水で希釈し0.1~0.2%濃度として、アルミトレーに1mm厚程度となるように入れ、80℃で乾燥し、これを電子顕微鏡で観察し、粒子径を測

定した。

電子顕微鏡：日本電子(株)製 走査型電子顕微鏡 model JSM-6300F

(2) 分子量

クロロホルムを溶媒として用い、25℃における極限粘度を測定して算出した。

【0022】(3) ガラス転移温度; Tg

Foxの式により求めた。なお、各単量体のTgは、ポリマーハンドブック/Wiley Interscienceの値を使用した。

(4) アイゾット衝撃強度(ノッチあり)

ASTM-D256に準拠して測定した。

(5) 熱変形温度; HDT

ASTM-D648(264psi)に準拠して測定した。

(6) 全光線透過率、ヘイズ

ASTM-D1003(5mm厚)に準拠して測定した。

【0023】(7) 成形加工性の評価

樹脂組成物の成形性及び加工性は、これをペレット化して射出成形機で3mm鏡面平板を成形することにより、また3本の鏡面ロールを備えた90 ϕ シート押出機で3mm押出板を製造し、次いでこれを加熱後突き上げ加工することにより評価した。

【0024】(実施例1)

(1) 多層構造重合体(A-1)ラテックスの製造

還流コンデンサー付き反応槽にイオン交換水150部、ステアリン酸ナトリウム0.4部、ラウリルサルコシン酸ナトリウム0.05部を仕込み、窒素雰囲気下で攪拌しながら80℃に昇温後、MMA24部、EA1部、ALMA0.05部からなる単量体混合物および1%KPS水溶液2.5部を仕込んで60分間反応させて重合を完了した。続いて1%KPS水溶液5部を仕込んだ時点で、BA41.3部、ST8.7部、ALMA1部からなる単量体混合物を60分間連続滴下して全量を仕込んだ後、60分間保持して重合を完了させた。次いで1%KPS水溶液を2.5部仕込んだ後、MMA24部、MA1部、n-OM0.05部からなる単量体混合物を40分間かけて全量を連続滴下し、さらに60分間保持して重合を完了させ多層構造重合体(A-1)ラテックスを得た。各層の重合終了後ラテックスをサンプリングし、電子顕微鏡観察で新しい粒子の生成がなく逐次重合が行われていることを確認した。得られたラテックスの粒子径は0.22 μ mであった。このラテックスの組成などを、表1の(A-1)に示す。

【0025】(2) 硬質メタクリル樹脂(B-1)ラテックスの製造

還流コンデンサー付き反応槽にイオン交換水150部、ステアリン酸ナトリウム1.2部、ラウリルサルコシン酸ナトリウム0.5部を仕込み、窒素雰囲気下で攪拌し

ながら75℃に昇温後、MMA47部、MA3部、n-OM0.13部からなる単量体混合物および1%KPS水溶液5部を仕込んで60分間反応させて重合を完了した。続いて1%KPS水溶液5部を仕込んだ時点で、MMA47部、MA3部、n-OM0.13部からなる単量体混合物を60分間連続滴下して全量を仕込んだ後、60分間保持して重合を完了させた。得られたラテックスの粒子径は0.12μmであった。このラテックスの組成などを、表1の(B-1)に示す。

【0026】(3)メタクリル系重合体(C-1)ラテックスの製造

還流コンデンサー付き反応槽にイオン交換水150部、ステアリン酸ナトリウム1.2部、ラウリルザルコシン酸ナトリウム0.5部を仕込み、窒素雰囲気下で攪拌しながら65℃に昇温後、MMA25部および1%KPS水溶液2部を仕込んで90分間反応させて重合を完了した。次いで1%KPS水溶液7.5部を仕込んだ時点で、MMA75部を100分間連続滴下し、全量を仕込んだ後90分間保持して重合を完了させた。得られたラテックスの粒子径は0.15μmであった。このラテックスの組成などを、表1の(C-1)に示した。

【0027】このようにして得られたそれぞれのラテックスを重合体換算で、多層構造重合体(A-1)60部、硬質メタクリル樹脂(B-1)35部およびメタクリル系重合体(C-1)5部をラテックス状態で均一混合した後、2%硫酸マグネシウム水溶液を添加して塩析凝固し、水洗・乾燥して重合体粉末を得た。得られた重合体粉末100部と硬質メタクリル系樹脂であるパラベットEHビーズ〔(株)クラレ製：押出成形用グレード、以下(D-1)と略称する〕100部を均一混合し、シート押出機により押出板とし、その諸物性を測定評価した。その結果を表2に示す。

【0028】(実施例2)

(1)多層構造重合体(A-2)ラテックスの製造

還流コンデンサー付き反応槽にイオン交換水150部、ジオクチルスルホコハク酸ナトリウム0.2部を仕込み、窒素雰囲気下で攪拌しながら85℃に昇温後、MMA33部、MA2部、ALMA0.15部からなる単量体混合物および1%KPS水溶液3.5部を仕込んで60分間反応させて重合を完了した。続いて1%KPS水溶液4.5部を仕込んだ時点で、BA36.5部、ST8.5部、ALMA1部からなる単量体混合物を60分間連続滴下して全量を仕込んだ後、60分間保持して重合を完了させた。次いで1%KPS水溶液2部を仕込んだ後、MMA19部、MA1部、n-OM0.05部からなる単量体混合物を40分間かけて全量を連続滴下し、さらに60分間保持して重合を完了させ多層構造重合体(A-2)ラテックスを得た。各層の重合終了後ラテックスをサンプリングし、電子顕微鏡観察で新しい粒子の生成がなく逐次重合が行われていることを確認し

た。得られたラテックスの粒子径は0.15μmであった。このラテックスの組成などを、表1の(A-2)に示した。

【0029】(2)硬質メタクリル樹脂(B-2)ラテックスの製造

還流コンデンサー付き反応槽にイオン交換水150部、ジオクチルスルホコハク酸ナトリウム0.6部を仕込み、窒素雰囲気下で攪拌しながら80℃に昇温後、MMA18部、EA2部、n-OM0.05部、および1%KPS水溶液2部を仕込んで40分間反応させて重合を完了した。続いて1%KPS水溶液8部を仕込んだ時点で、MMA72部、EA8部、n-OM0.2部からなる単量体混合物を90分間連続滴下して全量を仕込んだ後60分間保持して重合を完了させた。得られたラテックスの粒子径は0.07μmであった。このラテックスの組成などを、表1の(B-2)に示した。

【0030】(3)メタクリル系重合体(C-2)ラテックスの製造

還流コンデンサー付き反応槽にイオン交換水150部、ジオクチルスルホコハク酸ナトリウム0.5部を仕込み、窒素雰囲気下で攪拌しながら75℃に昇温後、MMA27部、MA3部、n-OM0.006部からなる単量体混合物、および1%KPS水溶液3部を仕込んで60分間反応させて重合を完了した。次いで1%KPS水溶液7部を仕込んだ時点で、MMA63部、EA7部、n-OM0.014部からなる単量体混合物を100分間連続滴下し、全量を仕込んだ後60分間保持して重合を完了させた。得られたラテックスの粒子径は0.12μmであった。このラテックスの組成などを、表1の(C-2)に示した。

【0031】このようにして得られたそれぞれのラテックスを重合体換算で、多層構造重合体(A-2)80部、硬質メタクリル樹脂(B-2)15部およびメタクリル系重合体(C-2)5部をラテックス状態で均一混合した後、-40℃で3時間掛けて凍結凝固させ、75℃の温水中で水を融解し、次いで脱水・乾燥して重合体粉末を得た。得られた重合体粉末100部と硬質メタクリル系樹脂であるパラベットHR-L〔(株)クラレ製：射出成形用グレード、以下(D-2)と略称する〕100部を均一混合してペレット化し、射出成形評価及び諸物性を評価した。その結果を表2に示す。

【0032】(実施例3～8)実施例1と同様の方法により、層数、組成、粒子径のそれぞれ異なる多層構造重合体(A-3)～(A-6)ラテックス、硬質メタクリル樹脂(B-3)ラテックス、およびメタクリル系重合体(C-3)ラテックスを得た。これら重合体の層数、組成、粒子径などを表1に示す。ラテックスブレンドでの各重合体の混合割合、ペレット化、シート化時の硬質メタクリル系樹脂との混合割合などを表2に示す他は実施例1と同様にし、得られた射出成形平板、押出板を測

定・評価した。その結果を表2に示した。

【0033】(比較例1~3)実施例での多層構造重合体ラテックス、硬質メタクリル樹脂ラテックスおよびメタクリル系重合体ラテックスを用いたが、ラテックスブレンドでの各重合体の混合割合が本発明の特許請求の範囲を逸脱した場合は、欠点の発生が認められ満足するものは得られなかった。その結果を表2に示した。

【0034】(比較例4)分子量の小さいメタクリル系*

*重合体(C-4)ラテックスを実施例と同様の方法により得、これと実施例での多層構造重合体ラテックス、および硬質メタクリル樹脂ラテックスとブレンドしが、欠点の発生が認められ満足するものは得られなかった。その結果を表2に示した。

【0035】

【表1】

| | 多層構造重合体(A)、硬質メタクリル樹脂(B)、メタクリル系重合体(C)の組成 [部] | 粒子径 [μm] | 分子量($\times 10^{-4}$)/Tg [°C] |
|-------|--|-------------|---------------------------------|
| (A-1) | MMA-EA-ALMA/BA -ST-ALMA/MMA-MA-n-OM 24 -1 -0.05/41.3-8.7-1 /24 -1 -0.05 | 0.22 | — |
| (A-2) | MMA-MA-ALMA/BA -ST-ALMA/MMA-MA-n-OM 38 -2 -0.15/36.5-8.6-1 /19 -1 -0.05 | 0.15 | — |
| (A-3) | BA -ST-ALMA/MMA-MA-n-OM 49.2-10.8-1 /38 -2 -0.08 | 0.08 | — |
| (A-4) | MMA-ALMA/BA-ST-ALMA/MMA-BA-ST-BGDM/MMA-MA-n-OM 25 -0.1 /41-9 -1 /4 -5 -1 -0.05 /14 -1 -0.03 | 0.31 | — |
| (A-5) | MMA-BA-ALMA/MMA-BA-n-OM 24 -6 -0.2 /62 -8 -0.33 | 0.06 | — |
| (A-6) | BA-BD/MMA-MA-n-OM 30-20/48 -2 -0.1 | 0.08 | — |
| (B-1) | MMA-MA-n-OM/MMA-MA-n-OM 47 -8 -0.13/47 -3 -0.13 | 0.12 | — |
| (B-2) | MMA-EA-n-OM/MMA-EA-n-OM 18 -2 -0.05/72 -8 -0.2 | 0.07 | — |
| (B-3) | MMA-MA-n-OM/MMA-MA-n-OM 39 -1 -0.16/58.5-1.5-0.24 | 0.18 | — |
| (C-1) | MMA/MMA 26 /75 | 0.15 | 18000/105 |
| (C-2) | MMA-MA-n-OM /MMA-MA-n-OM 27 -8 -0.006/63 -7 -0.014 | 0.12 | 4400/ 92 |
| (C-3) | MMA-EA/MMA-EA 22 -3/66 -9 | 0.08 | 11000/ 83 |
| (C-4) | MMA-MA-n-OM /MMA-MA-n-OM 24 -1 -0.02 /72 -3 -0.06 | 0.19 | 2700/100 |

[表中、横線(—)は同一層を形成するために用いられ※50※の単量体等を区別するために用い、また斜線(/)は層

が異なることを示すために用いた。]

*【表2】

【0036】

*

| | ラテックスブレンド | | | 押出溶融ブレンド | | Isod 衝撃強度 [kg-cm/cm] | HDT [°C] | 全光線 透過率 [%] | ヘイズ [%] | 成形性または加工性の評価 |
|------|-------------|-------------|-------------|------------|--------------|----------------------------|-------------|-------------------|------------|---------------------------------------|
| | (A) [部] | (B) [部] | (C) [部] | (C) [部] | (D) [部] | | | | | |
| 実施例1 | (A-1) 60 | (B-1) 35 | (C-1) 5 | — | (D-1) 200 | 4.1 | 98 | 92 | 1 | サージングなくシート成形性良好 突上げコーナー部の均一性良好 |
| 実施例2 | (A-2) 80 | (B-2) 10 | (C-2) 10 | — | (D-2) 100 | 7.2 | 96 | 92 | 1 | 射出成形性良好： ゲート部欠点なし |
| 実施例3 | (A-3) 98 | — | (C-3) 2 | — | (D-2) 70 | 9.8 | 83 | 92 | 1 | 射出成形性良好： ゲート部欠点なし |
| 実施例4 | (A-4) 40 | (B-3) 56 | (C-2) 4 | — | — | 5.5 | 85 | 92 | 1 | 射出成形性良好： ゲート部欠点なし |
| 実施例5 | (A-1) 70 | (B-1) 30 | — | (C-1) 5 | (D-2) 95 | 6.4 | 90 | 92 | 1 | 射出成形性良好： ゲート部欠点なし |
| 実施例6 | (A-1) 70 | (B-1) 20 | (C-1) 10 | — | (D-1) 200 | 2.1 | 92 | 92 | 1 | サージングなくシート成形性良好 突上げコーナー部の均一性良好 |
| 実施例7 | (A-5) 97 | — | (C-3) 3 | — | — | 3.1 | 58 | 91 | 2 | サージングなくシート成形性良好 突上げコーナー部の均一性良好 |
| 実施例8 | (A-6) 80 | (B-1) 15 | (C-3) 5 | — | (D-2) 100 | 13.4 | 90 | 92 | 1 | 射出成形性良好： ゲート部欠点なし |
| 比較例1 | (A-1) 60 | (B-1) 40 | — | — | (D-1) 200 | 3.9 | 94 | 92 | 1 | シート成形時サージング発生しやすい 突上げコーナーエッジ部均一性低下 |
| 比較例2 | (A-2) 80 | (B-2) 20 | — | — | (D-2) 100 | 6.8 | 89 | 92 | 1 | 射出成形性： ゲート部クモリ欠点発生 |
| 比較例3 | (A-3) 75 | — | (C-2) 25 | — | (D-2) 50 | 6.5 | 78 | 92 | 1 | 射出成形性： 流動性低下、成形不良 |
| 比較例4 | (A-1) 60 | (B-1) 30 | (C-4) 10 | — | (D-2) 200 | 4.2 | 98 | 92 | 1 | 射出成形性： ゲート部クモリ欠点発生 |

【0037】

【発明の効果】以上のように、本発明の耐衝撃性メタクリル系樹脂組成物は、上記構成を採用しているので、射出成形においては成形条件、金型ゲート形状等により成

※形品のゲート部にクモリ等の表面欠点のが発生がなく、またシート成形、フィルム成形あるいはシート加工においては板厚の偏りが少なく均一性が高く、表面荒れ等のない良好な製品を提供することができ、各種成形におい

(8)

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て好適に用いられる。